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Synthesis of nanocrystalline magnesium oxide by thermolysis of magnesium citrate

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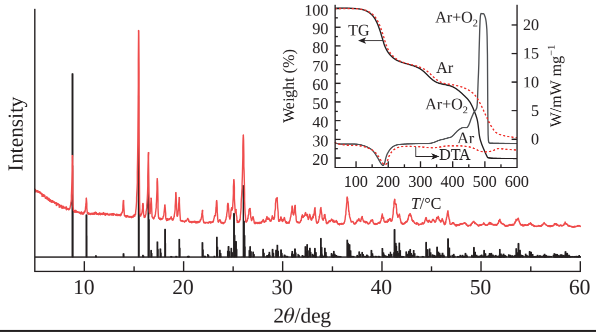
Magnesium citrate, obtained by dissolving magnesium oxide in an aqueous solution of citric acid, turned out to be a decahydrate of the composition $Mg_3(C_6H_5O_7)_2\cdot 10H_2O$, which was established by the results of synchronous thermal analysis, X-ray diffraction and IR spectroscopy. It is shown that the thermal decomposition of this salt proceeds in three stages in the temperature ranges of 120–250, 250–370 and 370–550 °C to form nanocrystalline magnesium oxide with grain sizes from 7 to 23 nm.



Keywords: magnesium citrate, $Mg_3(C_6H_5O_7)_2\cdot 10H_2O$, thermolysis mechanism, X-ray amorphous products, nanocrystalline magnesium oxide.

Among the various methods for obtaining mesoporous carbon materials, special attention is paid to template synthesis methods, which make it possible to provide materials with a given morphology and pore size,[1] while both micellar systems[2,3] and solid templates[4,5] can act as template agents. Nanocrystalline magnesium oxide can be used as a solid template for the synthesis of highly porous carbon materials.[6,7] Methods have been published for preparing porous carbon materials by mixing magnesium salts with various carbon precursors. During the synthesis of a carbon material, the magnesium salt decomposes to form magnesium oxide, which plays the role of a template agent. According to published data, salts such as magnesium acetate[8] and citrate[9] can be used for this purpose. Comparative data[6] have been published on the characteristics of carbon materials obtained from polyvinyl alcohol as a carbon precursor using magnesium acetate and magnesium citrate additives. It was possible to obtain carbon materials with a specific surface area of more than 1000 $m^2\ g^{-1}$, which are promising for use as adsorbents or electrode materials for electrochemical devices. Despite the promise of using magnesium salts as additives for the production of highly dispersed carbon materials, the mechanisms of thermolysis of these salts and the factors affecting the formation of nanocrystalline magnesium oxide formed during thermolysis have not yet been elucidated.

Magnesium citrate is an available and non-toxic compound widely used in medicine, which explains the choice of this compound as a functional additive in the synthesis of carbon materials.[1,9] To the best of our knowledge, in order to elucidate the mechanism of thermolysis and identify the products of thermolysis, only the crystal hydrate of magnesium citrate of the composition $Mg_3(C_6H_5O_7)_2\cdot 14H_2O$ with a known structure was studied.[10] Recently, the crystal structure of another citrate salt, magnesium citrate decahydrate $Mg_3(C_6H_5O_7)_2\cdot 10H_2O$, has been refined,[11] but no information on its thermolysis has been presented. In this work, magnesium citrate was synthesized in a simple and accessible way, and the thermolysis process and decomposition products of magnesium citrate obtained at various temperatures were investigated.

Magnesium citrate $Mg_3(C_6H_5O_7)_2\cdot xH_2O$ used in this study was obtained[†] by the reaction

$$\begin{aligned} &3\,MgO + 2\,(HOOCCH_2)_2C(OH)COOH + (x-3)\,H_2O = \\ &= Mg_3(C_6H_5O_7)_2\cdot xH_2O. \qquad (1) \end{aligned}$$

Figure 1(*a*) displays powder X-ray diffraction patterns of the obtained $Mg_3(C_6H_5O_7)_2\cdot xH_2O$. Comparison with the known data showed that the position of the reflections in the diffraction pattern of the obtained sample is in good agreement with the corresponding values for decahydrate $Mg_3(C_6H_5O_7)_2\cdot 10H_2O$. According to the results of X-ray diffraction studies obtained on

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[†] Magnesium oxide (MgO, 98% purity, 10 g), pre-calcined at 450 °C, was dissolved in small portions in an aqueous solution (100 ml) of 1.65 M citric acid (99.8% purity) at a temperature of 70 °C with intensive stirring. The precipitate obtained by evaporation of the resulting solution was dried at 70 °C for 2 h. As a result, a white powder of magnesium citrate crystal hydrate $Mg_3(C_6H_5O_7)_2\cdot xH_2O$ was obtained and characterized by the methods of physicochemical analysis. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a STA 449 F/1/1 JUPITER synchronous thermal analyzer at a heating rate of 10 K min^{-1} in a pure argon atmosphere and in a 60% Ar–40% O_2 mixture. In parallel, the ion current of the mass spectrometric sensor was measured for mass numbers M = 18 c.u. and M = 44 c.u., corresponding to the concentration of water and carbon dioxide released during thermolysis, respectively. X-ray diffraction patterns of magnesium citrate and its thermolysis products were obtained on a Bruker D8 Advance diffractometer using CuKα (λ = 1.542 Å) radiation in the 2θ angle range from 5° to 60°. The surface characteristics of the obtained magnesium oxide were evaluated from BET nitrogen adsorption/desorption isotherms using a 5-point method at 77 K on a Thermosorb TPD1200 surface analyzer.

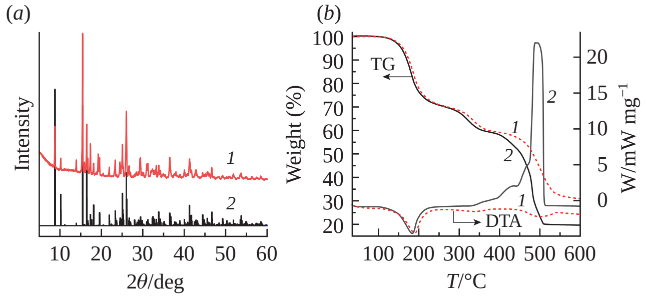

Figure 1 (*a*) Comparison of (*1*) the measured X-ray diffraction pattern of the initial $Mg_3(C_6H_5O_7)_2 \cdot xH_2O$ sample with (*2*) the theoretical X-ray diffraction pattern of $Mg_3(C_6H_5O_7)_2 \cdot 10H_2O$ plotted according to known data.[12] (*b*) TG and DTA curves of thermolysis of $Mg_3(C_6H_5O_7)_2 \cdot 10H_2O$ salt in (*1*) argon atmosphere and (*2*) argon–oxygen mixture.

a $Mg_3(C_6H_5O_7)_2 \cdot 10H_2O$ single crystal,[11] this compound has a monoclinic crystal lattice (space group $P2_1/n$) with unit cell parameters $a = 20.222$, $b = 6.686$ and $c = 9.135$ Å, $\beta = 96.86°$.

Figure 1(*b*) shows the results of thermal analysis obtained by heating samples of the initial $Mg_3(C_6H_5O_7)_2 \cdot xH_2O$ in an atmosphere of pure argon and in a mixture of 60% argon–40% oxygen. Figure 2(*a*),(*b*) shows the temperature dependences of the ion current of the mass spectrometric sensor, corresponding to the release of gaseous water and carbon dioxide from the same samples. It can be seen that salt thermolysis occurs in three stages at temperatures of 120–250 (I), 250–370 (II) and 370–550 °C (III). Each stage is accompanied by a change in the weight of the sample, and the change in weight and thermal effects in the first two stages are identical when heated in inert and oxidizing atmospheres.

At stage I of thermolysis, weight loss occurs, accompanied by an endothermic effect, which corresponds to the course of the dehydration reaction

$$Mg_3(C_6H_5O_7)_2 \cdot 10\,H_2O = Mg_3(C_6H_5O_7)_2 + 10\,H_2O. \tag{2}$$

Dehydration is confirmed by the presence of an intense peak of the ion current caused by the release of water vapor. The calculated weight change during the reaction is 28.5% (the residual product fraction is 71.5%), which is close to the observed value. Taking into account the above data of X-ray diffraction studies, it can be concluded that the initial sample is a pure decahydrate of the composition $Mg_3(C_6H_5O_7)_2 \cdot 10H_2O$. Figure 3 shows powder X-ray diffraction patterns of thermolysis products obtained at different temperatures. The powder diffraction pattern of the product obtained after heating at 250 °C does not contain peaks related to crystalline phases, which indicates the amorphous structure of the dehydrated product.

At stage II, a further decrease in weight occurs, which can be explained by the decomposition of magnesium citrate with the formation of amorphous phases based on magnesium aconitate [magnesium prop-1-ene-1,2,3-tricarboxylate, $Mg_3(C_6H_3O_6)_2$], magnesium itaconate [magnesium 2-methylidenebutanedioate, $Mg(C_5H_4O_4)$], magnesium citraconate [magnesium (2*Z*)-2-methylbut-2-enedioate, $Mg(C_5H_4O_4)$], or both, as well as magnesium carbonate ($MgCO_3$):

$$Mg_3(C_6H_5O_7)_2 = Mg_3(C_6H_3O_6)_2 + 2\,H_2O, \tag{3}$$

$$Mg_3(C_6H_3O_6)_2 = Mg(C_5H_4O_4) + 2\,MgCO_3 + (2/y)\,C_xH_y + CO_2 + (4-2x/y)\,C. \tag{4}$$

Reaction (3) is accompanied by the release of water vapor, which is confirmed by the presence of an ion peak on the thermogram. The release of carbon dioxide is caused by a parallel reaction (4). The presence of magnesium aconitate in the products of the thermolysis of magnesium citrate was noted earlier.[10] It has been previously shown that thermolysis of magnesium aconitate yields magnesium itaconate and citraconate.[13] As can be seen from the diffraction pattern [Figure 3(*a*), curve *2*], the thermolysis products remain amorphous after heating at 370 °C, *i.e.*, magnesium carbonate does not crystallize into a separate phase, but remains as part of the amorphous products. The change in weight in the inert atmosphere in the temperature range of 250–370 °C is 58.5% and can be quantitatively described by parallel reactions (3) and (4). The weight loss when measured in the oxidizing atmosphere is slightly greater, which is explained by the partial oxidation of thermolysis products, which becomes noticeable at temperatures above 350 °C and is accompanied by an exothermic effect.

Stage III of thermolysis proceeds at temperatures of 370–550 °C and is different for thermolysis in inert and oxidizing atmospheres. In an inert argon atmosphere, a further decrease in the weight of the sample is observed, accompanied by an endothermic effect. The most probable processes at this stage are the thermolysis of organic magnesium salts with the formation of magnesium carbonate,

$$Mg(C_5H_4O_4) = MgCO_3 + CO + (4/y)\,C_xH_y + (3-4x/y)\,C, \tag{5}$$

and decomposition of magnesium carbonate to form nanocrystalline magnesium oxide,

$$MgCO_3 = MgO + CO_2. \tag{6}$$

The overall process of complete thermolysis of magnesium citrate decahydrate in an inert atmosphere can be represented by the reaction

$$Mg_3(C_6H_5O_7)_2 \cdot 10\,H_2O = 3\,MgO + 4\,CO_2 + 12\,H_2O + CO + (7-6x/y)\,C + (6/y)\,C_xH_y. \tag{7}$$

The relative residual weight of the product calculated for reaction (7) is 32.5%, which is close to the experimental value of 31.0%. The slight difference between the experimental value and the calculated one can be explained by the possibility of the formation of gaseous hydrocarbons, leading to a decrease in the

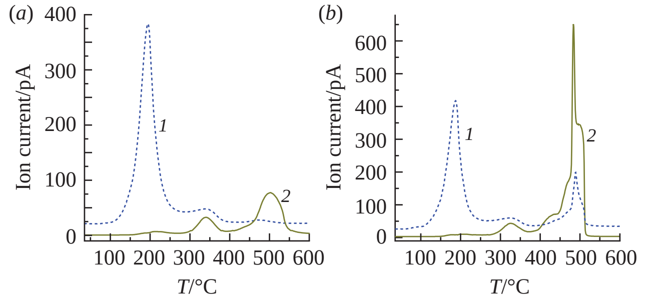

Figure 2 Temperature dependences of the ion current corresponding to the concentrations of (*1*) water and (*2*) carbon dioxide in the gas phase, obtained by synchronous thermal analysis during the thermolysis of magnesium citrate in (*a*) an atmosphere of pure argon and (*b*) an argon–oxygen mixture.

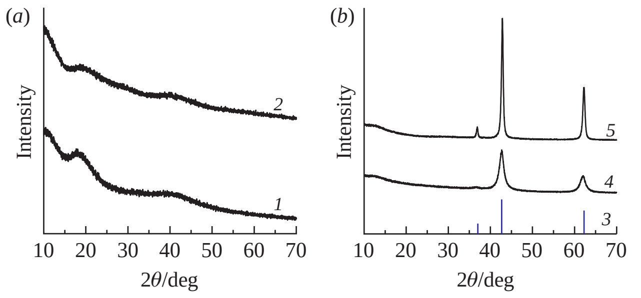

Figure 3 Powder X-ray diffraction patterns of magnesium citrate thermolysis products formed (*a*) at stages I and II after heating at (*1*) 250 and (*2*) 370 °C, respectively, and (*b*) at stage III after heating at (*4*) 480 and (*5*) 550 °C, in comparison with (*3*) the theoretical diffraction pattern of MgO constructed according to the PDF-2 database (file no. 1-257).

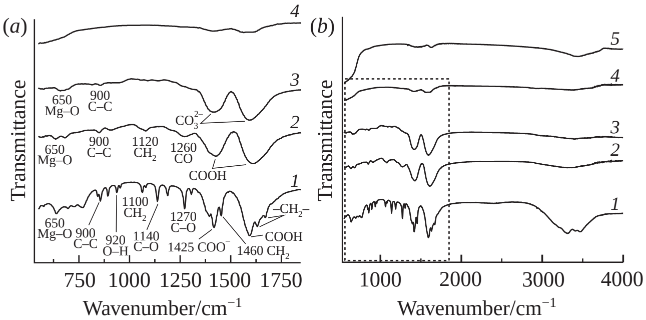

Figure 4 IR spectra of (*1*) the initial magnesium citrate and products of its heating at (*2*) 250, (*3*) 370, (*4*) 480 and (*5*) 550 °C in the spectral ranges of (*a*) 600–1800 and (*b*) 600–4000 cm^{-1}.

amount of elemental carbon in the residual product. The overall process of thermolysis in an oxidizing oxygen–argon atmosphere is described by the reaction equation

$$Mg_3(C_6H_5O_7)_2 \cdot 10H_2O + 9\,O_2 = 3\,MgO + 12\,CO_2 + 15\,H_2O. \quad (8)$$

In this case, the relative residual weight is 19.7%, which practically coincides with the theoretical value of 19.2%.

As can be seen from the diffraction patterns [Figure 3(*b*), curves *4* and 5], magnesium oxide formed as a result of thermolysis has a periclase structure (file no. 1-251, PDF-2 database) and is nanocrystalline, as evidenced by a noticeable broadening of reflections. The grain size (more precisely, the coherent scattering regions), determined by the Debye–Scherrer method, is 7.2 ± 0.1 nm and 23.8 ± 0.2 nm for samples heated at 480 and 550 °C, respectively.

The specific surface area of the samples was determined by analyzing nitrogen adsorption isotherms by the BET method. The specific surface area of the samples obtained by the thermal decomposition of magnesium citrate at 480 and 550 °C is 231 and 70 m^2 g^{-1}, respectively, which is in good agreement with the data calculated from the grain size estimated from X-ray diffraction data.

Figure 4 shows the IR spectra of the initial sample and thermolysis products at different temperatures. The IR spectrum of the initial sample contains absorption bands at 3311 and 3470 cm^{-1}, which indicates the presence of O–H and C–H bonds, absorption bands at 1450 and 1610 cm^{-1} indicate the presence of carboxyl groups, and absorption bands in the range from 600 to 1400 cm^{-1} can be attributed to the vibration frequencies of the C–C, C–H and C–O bonds. By identifying the absorption bands of a sample heated at 250 °C, one can speak of the removal of water, which is indicated by the almost complete disappearance of a broad peak in the region of 3000–3600 cm^{-1}. The main peaks characteristic of magnesium citrate are retained. At the same time, the peak at 1140 cm^{-1} related to the vibration frequency of the alcohol OH group of the citrate anion disappears. This indicates the transformation of magnesium citrate into magnesium aconitate, itaconate and citraconate during prolonged thermal exposure of the sample at 250 °C. The formation of aconitate under these conditions is indicated in the published work.[11] In the IR spectrum of the sample heated at 370 °C, there are almost completely no peaks corresponding to functional groups with C–H and C–O bonds. Along with this, broad intense absorption bands at 1450 and 1610 cm^{-1} are preserved, which correspond to the vibration frequencies of C–O bonds in carboxyl groups and carbonate anions. Apparently, at this stage of thermolysis, the formation of magnesium itaconate/citraconate and amorphous magnesium carbonate is completed in accordance with reactions (3) and (4), however, the bands corresponding to these compounds overlap at these frequencies with the bands of the carboxyl group of aliphatic compounds, and their resolution using IR spectroscopy is difficult. For the sample heated at 480 °C, a decrease in the intensity of the bands at 1450 and 1610 cm^{-1} is observed, due to the decomposition of magnesium carbonate to the corresponding oxide, as evidenced by the appearance of a band at frequencies less than 500 cm^{-1}. The IR spectrum of the thermolysis products of magnesium citrate obtained after heating at 550 °C is characterized by the presence of bands corresponding to pure magnesium oxide. In general, the changes observed in the IR spectra of the thermolysis products are in good agreement with the data obtained by TG, DTA and X-ray diffraction analysis and confirm the proposed mechanism of thermolysis.

Thus, magnesium citrate decahydrate $Mg_3(C_6H_5O_7)_2 \cdot 10H_2O$ was synthesized in this work. Its diffraction pattern agrees with the published data, and its chemical composition is confirmed by thermogravimetric data. Synchronous thermal analysis and X-ray diffraction analysis showed that the thermolysis reaction of magnesium citrate decahydrate proceeds in three stages. At the first stage, in the temperature range of 120–250 °C, dehydration of magnesium citrate occurs. At the next stage, at 250–370 °C, magnesium citrate decomposes to form amorphous phases based on magnesium aconitate [magnesium prop-1-ene-1,2,3-tricarboxylate, $Mg_3(C_6H_3O_6)_2$], magnesium itaconate [magnesium 2-methylidenebutanedioate, $Mg(C_5H_4O_4)$], magnesium citraconate [magnesium (2*Z*)-2-methylbut-2-enedioate, $Mg(C_5H_4O_4)$], or both, and magnesium carbonate ($MgCO_3$). At temperatures of 370–550 °C, the final decomposition of the mixture takes place. In an inert atmosphere, a mixture of magnesium oxide and carbon is formed, and in an oxidizing atmosphere, the only decomposition product is magnesium oxide. The results of thermal analysis and the proposed scheme of thermolysis are confirmed by the analysis of the IR spectra of the samples obtained by heating magnesium citrate at different temperatures. Magnesium oxide obtained by thermolysis is nanocrystalline and can be used as a solid template in the synthesis of mesoporous carbon materials.

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